CHIral Saddle-shaped Organic Semiconductors (CHISOS)

a) Consortium/Partnership:

Dr. K. Dhbaibi & **Pr. D. Kreher** (ED 2MIB, UVSQ/ILV/SORG team), **project leaders**, respectively **PhD Director** & **principal supervisor**, david.kreher@uvsq.fr; **Dr. C. Barreteau** (ED EDOM, CEA Paris-Saclay/IRAMIS/SPEC/GMT group), **PhD co-Director** & **partner 1**, cyrille.barreteau@cea.fr; **Dr. G. Pieters** (ED 2MIB, CEA Paris-Saclay/SCBM), **partner 2**, gregory.pieters@cea.fr; **Pr. C. Adachi** (OPERA/Kyushu University, Japan), **partner 3**.

b) Context of CHISOS project

Chirality, which refers to right- or left-handedness, has been extensively studied in various fields, but despite its well-recognized role in biological functions, chirality remains underexplored in materials science. An intriguing property of chiral molecules is their ability to interact specifically with left- and right-handed circularly polarized light, either in absorption (Electronic Circular Dichroism, ECD) or emission (**Circularly Polarized Luminescence**, **CPL**). The latter phenomenon is now at the forefront of various photonic applications, including 3D displays, anti-counterfeiting systems, and circularly polarized (CP) bioimaging and detection.[1] For a long time, lanthanide complexes have been the preferred class for CPL studies due to their large **luminescence dissymmetry factors** (g_{lum}>1),[2] but small chiral organic molecules gained interest as emitters for their tunable photophysical/chiroptical properties, as well as their easier integration into chiro-optoelectronic devices. While these molecules offer higher luminescence quantum yields, their much lower g_{lum} values (10^{-4}-10^{-2}) limit their use in real-world technological applications.[3] **Expanding the library of organic chiral emitters** and establishing **comprehensive structure–property relationships** is crucial for designing efficient emitters and advancing this field further.

c) Objectives and scientific impact of CHISOS project

In this work, we will explore the synthesis and photophysical/chiroptical properties of new families of enantioenriched chromophores based on an original combination of Cyclooctatetraphenylene (COTPh)[4] or Cyclooctatetrathiophene (COTTh)[5] and porphyrin pigments. This association will give rise to novel 3D organic semiconductors (OSCs) merging multiple desirable properties, including remarkable solubility, good thermal and chemical stability, and significant chiroptical activity, as a result of the synergistic interaction between the saddle-shaped core and the pigment properties (***Fig. 1***). When the saddle-shaped structure combines with the extensive π-conjugation in a given organic π-conjugated system, it promotes balanced charge mobility and favourable morphology.[6] Various strategies will be employed to modulate chiroptical properties in both the ground and excited states. These strategies include altering functionalization positions, varying the number of porphyrin units incorporated, and modifying the nature of the metal center in the porphyrin core. CPL activity in the far-red region is anticipated due to the exciton coupling chirality mechanism between the electric dipole-allowed transition moments of the π-π* transitions in the porphyrin dyes.[7] Moreover, excellent CPL brightness (B_{CPL}) is expected, owing to the high molar absorptivity of the porphyrin unit.[8]

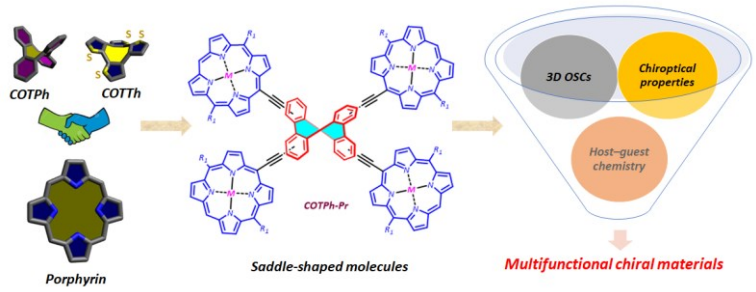

Fig. 1. Multifunctional chiral material based on the association of saddle-shaped COTPh or COTTh with porphyrin.

d) Interdisciplinary dimension and approaches of CHISOS project

The project offers a wide range of perspectives with significant scientific impact and both an interdisciplinary and international dimension, addressing various aspects: i) **bridging**

experiments and theory: Density functional theory (DFT) will be used by **partner 1** to model the electronic structure of various classes of chiral molecules.[9] This approach will enable a fine-characterization of the transition magnetic dipole moments, transition electric dipole moments, and the angle between them. This will help us both to select the most promising targets to be synthetized by **project leaders** (***Fig. 2)*** and to optimize chiroptical activities via **symmetry-based rational design.** *ii*) **multi-chiroptical characterization**: the chiroptical properties will be examined through ECD, CPL and VCD measurements with the expertise of **partner 2**:[10] this complementary and multifaceted analysis of optical activities will provide a comprehensive understanding of the structure–property relationships in enantioenriched molecules *iii)* **from rational design to real-world applications:** the ultimate goal of this project is not only to create a new library of optically active (COTPh) and (COTTh) molecules with unique chiroptical properties but also to deliver meaningful scientific contributions across multiple fields: in particular, we believe they could serve as active materials for emitting dissymmetric CPL in organic light-emitting diodes (**CP-OLEDs**),[11] which explains the presence in the consortium of **partner 3**.[12] In addition, if accepted, this innovating project would strengthen the recently-existing collaboration in the framework of the France/Japan **CNRS International Research Project (IRP) LUX-ERIT"** the project leaders belong to. We must emphasize also that the negatively curved architectures of our saddle-shape molecules offer also a promising avenue for **high-performance multifunctional chiral materials** after modulating their chiroptical properties *via* supramolecular host-guest interaction with fullerene guest.[13]

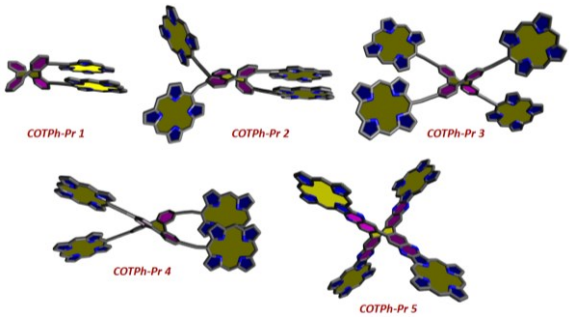

Fig. 2. 3D organic semiconductor structures based on cyclooctatetraene.

e) Methodology and quality-complementarity of the supervision

Pr. Kreher (Orcid n° 0000-0002-0968-5224) is an expert in the synthesis of π-conjugated functional molecular materials for optoelectronics applications. He co-supervised/ directed 24 PhD students, led or participated to 8 ANR projects among many other types. In addition, he was elected to join many scientific committees (CNRS, …), on parallel to managing his own research axis. Helped by a recently hired (2024) associate professor, *i.e.* Dr. Dhbaibi, both will benefit of the well-equipped synthesis facilities and numerous analytic techniques present at ILV. Together and with Dr. Barreteau (Orcid n° 0000-0002-9635-3884) as a co-director, they will dedicate at least 20% of their time to the present project, benefiting from the complementary skills of the other partners. To sum-up, **this multidisciplinary and international scientific environment (IRP) combining modelling, design and synthesis, photophysical and chiroptical characterizations, as well as the study of targeted emissive materials in CP-OLED devices, will fully benefit the doctoral student who would join this consortium,** with several months already planned and funded for his/her training in Japan.

f) References

[1] J. Crassous, M. J. Fuchter, D. E. Freedman, N. A. Kotov, J. Moon, M.C. Beard, S. Feldmann, *Nat. Rev. Mater*. **2023**, *8*, 365. [2] Zinna, F, Di Bari, L. *Chirality*. **2015**, 27, 1-13. [3] Y. Zhang, S. Yu, B. Han, Y. Zhou, X. Zhang, X. Gao, Z. Tang, *Matter*, **2022**, *5*, 837. [4] W. S. Rapson, R. G. Shuttleworth, J. N. van Niekerk, *J. Chem. Soc*. **1943**, 326. [5] M. Ueda, K. Jorner, Y. M. Sung, T. Mori, Q. Xiao, D. Kim, H. Ottosson, T. Aida, Y. Itoh, *Nat Commun.,* **2017**, *8*, 346. [6] Y. Wang, Y. Zhang, S.Wang, D. Cao, *Chem. Eur. J*. **2021**, *27*, 12012. [7] N. Berova, L. D. Bari, G. Pescitelli, *Chem. Soc. Rev.* **2007**, *36*, 914. c) G. Pescitelli, *Chirality*. **2022,** 34, 333. [8] L. Arrico, L. Di Bari, F. Zinna, *Chem. Eur. J.* **2021**, *27*, 2920. [9] Sven Johannsen, Manuel Gruber, Cyrille Barreteau, Maksym Seredyuk, José Antonio Real, Troels Markussen, and Richard Berndt. *J. Phys. Chem. Lett*. **2023**, 14, 7814. [10] M. Coehlo, L. Frédéric, L. Poulard, N. Ferdi, L. Estaque, A. Desmarchelier, G. Clavier, J-P Dognon, L. Favereau, M. Giorgi, J-V Naubron, G. Pieters, *Angew. Chem. Int. Ed*. **2024**, e202414490. [11] X. Wu, X. Yan, Y. Chen, W. Zhu, P.-T. Chou, *Trends Chem*. **2023**, *5*, 734. [12] X. Tang, T. Tsagaantsooj , T. P. B. Rajakaruna1, K. Wang, X-K. Chen, X-H. Zhang, T. Hatakeyama and C. Adachi 1.*Nat Commun*, **2024**, 15, 4394. [13] C.-L. Deng, X.-S. Peng, H. N. C. Wong, *Tetrahedron*. **2017**, *73*, 3606.